

PROCESS FOR PRODUCTION AND DISTRIBUTION OF A
PREREDUCED SELECTIVE HYDROGENATION CATALYST

5 Cross reference to related applications

NONE

Background of Invention

Field of Invention

10 This invention relates to a process for the production
and distribution of a prerduced selective hydrogenation
catalyst for use in an olefinic feed stream. This invention
also relates to a process of use of a prerduced
hydrogenation catalyst for the selective hydrogenation of an
olefinic feed stream.

15 **Prior Art**

20 The manufacture of unsaturated hydrocarbons usually
involves cracking various types of hydrocarbons and often
produces a crude product containing hydrocarbon impurities
that are more unsaturated than the desired product. These
unsaturated hydrocarbon impurities are often very difficult
to separate by fractionation from the desired product. A
common example of this problem occurs with ethylene
purification, in which acetylene is a common impurity. It
is often difficult, industrially, to remove such
25 undesirable, highly unsaturated hydrocarbons without
significant hydrogenation of the desired hydrocarbons. One
example of this process is described in UK Pat. No.
916,056.

Two general types of gas phase selective hydrogenation processes for removing undesired, unsaturated hydrocarbons have come into use. One, known as "front-end" hydrogenation, involves passing the crude gas from the initial cracking step, after removal of steam and condensable organic material, over a hydrogenation catalyst. Despite the large hydrogen content of such gas, which is very greatly in excess of the quantity of acetylenes that are present and which quantity should be sufficient to hydrogenate a substantial part of those acetylenes, substantially complete hydrogenation of the acetylenes with sufficient selectivity to produce olefins of polymerization quality is often a problem. The high concentration of hydrogen present in the front-end systems requires a very selective catalyst that does not also substantially hydrogenate the ethylene that is also present in the feed stream. Overhydrogenation can lead to thermal excursion known as "run-away". Under "run-away" conditions, high temperatures are experienced, severe loss of ethylene occurs and catalyst damage takes place. In addition, furnace upsets in the front-end reactor system can result in swings of CO concentration from moderate levels to very low levels. Existing front-end catalysts cannot tolerate these substantial swings in CO concentration very well and often are prone to "run-away". In a front-end reactor system, the

catalyst is also exposed to high space velocity operations of about 10,000-12,000 GHSV per bed.

In the other type of gas phase selective hydrogenation, known as "tail-end" hydrogenation, the crude gas is fractionated and the resulting concentrated product streams are individually reacted with hydrogen in a slight excess over the quantity required for hydrogenation of the unsaturated acetylenes which are present. Tail-end reactor systems operate at a GHSV of 2500-5000 per bed. In tail-end hydrogenation there is a greater tendency for deactivation of the catalyst during the hydrogenation procedure, and consequently, periodic regeneration of the catalyst is necessary. While the amount of hydrogen and carbon monoxide addition can be adjusted to maintain selectivity, formation of polymers is a major problem.

A number of patents have discussed the selective hydrogenation of unsaturated hydrocarbons such as U.S. Patent Nos. 4,126,645, 4,367,353, 4,329,530, 4,347,392 and 5,414,170.

The catalysts that are preferred for selective hydrogenation reactions generally comprise palladium supported on an alumina substrate, as disclosed, for example, in U.S. Patent Nos. 3,113,980, 4,126,645 and 4,329,530. Other gas phase palladium on alumina catalysts for the selective hydrogenation of acetylene compounds are

disclosed, for example, in U.S. Patent Nos. 5,925,799, 5,889,138, 5,648,576 and 4,126,645.

One of the problems that frequently occurs with palladium on alumina catalysts is that under normal operating conditions not only is the acetylene hydrogenated, a substantial portion of the ethylene is also converted to ethane. In addition, these palladium on alumina catalysts often have relatively low stability over extended periods of use due to the formation of large quantities of oligomers on the catalyst surface. To overcome this problem, enhancers or additives are often added to the palladium catalyst to improve its performance. One common additive is silver. For example, acetylene hydrogenation catalysts for ethylene purification comprising palladium and silver on a support material are disclosed in U.S. Patent Nos. 4,404,124, 4,484,015, 5,488,024, 5,489,565 and 5,648,576. In one specific example U.S. Patent No. 5,648,576 discloses a selective hydrogenation catalyst for acetylene compounds comprising from about 0.01 to 0.5 weight percent of palladium and from about 0.001 to 0.02 percent by weight of silver. 80 percent or more of the silver is placed within a thin layer near the surface of the carrier body.

Catalysts comprising palladium, silver, an alkali metal fluoride and a support material, which are utilized for the hydrogenation of other feed stream impurities, such as

dienes and diolefins, are disclosed, for example, in U.S. Patent No. 5,489,565.

Catalysts comprising palladium and gold on a catalyst support which may be used for the hydrogenation of acetylenes and diolefins have been suggested by U.S. Patent Nos. 4,533,779 and 4,490,481. These patents disclose the use of a substantially greater amount of palladium than of gold, specifically 0.03 to about 1 percent by weight palladium and from 0.003 to 0.3 percent by weight gold.

While conventional palladium or silver/palladium catalysts for the selective hydrogenation of acetylene have been useful, there are still a number of problems encountered when they are used, including a relatively low tolerance to carbon monoxide concentration swings, lower selectivity than is desirable by the industry, and problems with high space velocity operations.

The manufacturing process for silver and palladium hydrogenation catalysts generally includes reduction of the metallic oxides to their elemental states. However, because the silver and the palladium on these promoted catalysts reoxidize quite easily during conventional preparation, transportation, installation and use, for optimum performance it is necessary to again reduce the palladium and palladium/silver in the promoted catalysts in situ before selective hydrogenation of the acetylene can occur.

Because hydrogen pre-reduction in situ is not readily available in most commercial plants, catalyst activation with feed stock is the most common method of reduction in situ.

5 In the typical process for the preparation of a hydrogenation catalyst, particularly a palladium or silver/palladium catalyst, a carrier material, such as alpha alumina, is impregnated with a palladium compound, such as palladium chloride and, when silver is used as an additive, 10 a silver compound such as silver nitrate. See, for example, U.S. Patent No. 4,404,124.

15 The impregnated catalyst precursor material is then dried. While the material may then be used directly as a catalyst for hydrogenation, it is generally reduced prior to the drying step, often by wet reduction. After wet reduction the catalyst is washed to remove halides and dried. This drying step, which is normally conducted under air, generally reoxidizes the palladium and/or palladium/silver on the catalyst. After drying the catalyst 20 is packaged and shipped to the customer without further processing. Thus, before the catalyst can be utilized for selective hydrogenation, the metallic oxides must be reduced in situ. For this in situ reduction step to be successful, the feed for the selective hydrogenation process must 25 generally be modified from a conventional feed.

Conventionally, the reduction step requires an increase in the amount of hydrogen which is present in the feed stream.

The industry has determined that reduction of the hydrogenation catalyst in situ with feed stock is an acceptable procedure which avoids the expenses associated with installing costly hydrogen reduction facilities.

Processes for the reduction of the catalyst in situ are disclosed, for example, in U.S. Patent Nos. 4,329,530, 4,577,047, 4,551,443, 4,404,124, 4,410,455 and 4,577,047.

See also U.S. Patent No. 5,955,397. Thus, the recognized process for the reduction of the active metal or metals on a selective hydrogenation catalyst is at the plant in situ where the selective hydrogenation process is conducted.

Difficulties are often experienced in this in situ reduction process during normal operations. It has been discovered that the normal temperature of the feed stream is not generally high enough to effectively reduce metal oxides that are present on prior art catalysts. In addition, the presence of carbon monoxide in a front end ethylene purification feed stream inhibits the in situ activation of the catalyst, thus necessitating a higher temperature for the feed to successfully hydrogenate the appropriate materials. Such higher temperatures reduce the performance of the catalyst and reduce its life expectancy. That the presence of carbon monoxide in the feed stream would inhibit

reduction of the selective hydrogenation catalysts is surprising as carbon monoxide is often utilized as a reducing agent.

5 An additional problem with in situ reduction is that many of the existing plant reactors are not fitted with the equipment necessary to perform effective in situ activation of the catalyst prior to the introduction of the feed stock. Therefore, the feed stock must be utilized to reduce the catalyst. Because the catalyst has not yet been reduced 10 when the feed stock initially contacts the catalyst, there is a reduction in the performance of that catalyst until sufficient hydrogen has passed over the catalyst to reduce the metal oxides located on the catalyst. Thus, in situ reduction is frequently inefficient, resulting in 15 substandard performance of the catalyst.

Processes have been disclosed for the off site, wet reduction of catalyst material, for example as disclosed in U.S. Patent No. 4,367,167. However, these off site, wet reduction processes ultimately result in unreduced catalysts 20 because the wet reduced catalysts must be dried before they can be used in situ. As drying of the wet reduced catalyst is commonly conducted in air, the metals on the catalyst frequently reoxidize.

The processes of the invention are designed to address 25 these problems and deficiencies in conventional catalytic

hydrogenation reactions.

Accordingly, it is an object of this invention to disclose a process for the production of a catalyst for the selective hydrogenation of an olefinic feed stream containing acetylenic impurities.

It is a still further object of this invention to disclose a process for the production of a catalyst for the front-end and tail-end selective hydrogenation of acetylenic impurities, whereby the quantity of the desirable C_2 and C_3 olefins is not substantially reduced.

It is a still further object of this invention to disclose a process for the production of a catalyst for the front end and tail end selective hydrogenation of a C_2 and C_3 olefinic feed stream containing acetylenic impurities even when the quantity of carbon monoxide in the feed stream is high.

It is a still further object of the invention to disclose a catalyst for use in the selective hydrogenation of acetylenic impurities which is reduced prior to shipment to the end user.

It is a further object of the invention to disclose a catalyst for selective hydrogenation of acetylenic impurities prepared by an ex situ reduction process, whereby the temperature of reduction is controlled.

It is a still further object of the invention to

disclose an ex situ reduced palladium-based selective hydrogenation catalyst for the selective hydrogenation of acetylene which exhibits enhanced selectivity and reduced polymer formation over conventional palladium-based selective hydrogenation catalysts in front-end and tail-end reactor systems.

It is a further object of the invention to disclose a process for the production of palladium and palladium/silver catalysts for the selective hydrogenation of acetylene, wherein the palladium and/or palladium and silver on the catalysts are reduced ex situ.

It is a still further object of the invention to disclose a process for the ex situ reduction of palladium and palladium/silver selective hydrogenation catalysts useful for the selective hydrogenation of acetylene, which catalysts exhibit enhanced selectivity, resistance to run-away, tolerance to CO concentration swings and improved performance at high gas hourly space velocity over conventional palladium and palladium/silver selective hydrogenation catalysts.

These and other objects can be obtained by the processes for the preparation of an ex situ, reduced selective hydrogenation catalysts for use in a C_2 and C_3 olefinic feed streams containing acetylenic impurities which is disclosed by the present invention.

Summary of the Invention

The present invention is a process for the production and distribution of a catalyst for the selective hydrogenation of acetylenic impurities in an olefinic feed stream comprising

preparing a carrier material in a suitable shape;

impregnating the carrier material with a palladium compound;

calcining the carrier material impregnated with the palladium compound;

prereducing the palladium compound to a metallic state to form a palladium catalyst;

packaging the prereduced palladium catalyst under a non-oxidizing material in a storage container; and

distributing the prereduced palladium catalyst contained in a storage container to a customer for use in a process for selective hydrogenation of the olefinic feed stream, whereby the prereduced palladium catalyst is not again reduced prior to utilization on stream.

The present invention further comprises a prereduced palladium catalyst for hydrogenation prepared by the process described above. The catalyst of the present invention may also include silver as an additive.

The invention further comprises a process for the selective hydrogenation of acetylenic impurities contained

in an olefinic feed stream comprising passing the feed stream, which contains the acetylenic impurities, over a prereduced catalyst prepared by the process described above.

5

Detailed Description

The invention is a process for the production of a prereduced catalyst for selective hydrogenation. The invention is also a process for selective hydrogenation of a feed stream using the prereduced catalyst of the invention. The invention further comprises a catalyst produced by the process of the invention that is useful for selective hydrogenation. The catalyst of the invention is designed primarily for selective hydrogenation procedures, preferably of acetylene in admixture with ethylene.

15

A front end reactor feed stream for such selective hydrogenation procedures normally includes substantial quantities of hydrogen, methane, ethane, ethylene, carbon monoxide and carbon dioxide, as well as various impurities, such as acetylene. The goal of selective hydrogenation is to reduce substantially the amount of the acetylene present in the feed stream without substantially reducing the amount of ethylene that is present. If substantial hydrogenation of the ethylene occurs, thermal run-away can also occur.

20

25

The catalyst prepared by the process of the invention exhibits improved selectivity, resistance to run-away,

tolerance to CO concentration swings and improved performance at higher gas hourly space velocities (GHSV) over prior art selective hydrogenation catalysts. In addition to utilization for front-end purification, the catalyst of the invention is also useful for tail-end ethylene purification where the catalysts exhibit improved selectivity and reduced polymer formation. The process of prereduction of the catalyst ex situ is critical to the enhanced performance of hydrogenation catalysts of the invention.

The catalyst that is useful for this improvement in the selective hydrogenation process is comprised of a catalyst carrier onto which palladium is impregnated. In addition to palladium, other metals such as silver, tin copper, gold, lead, thallium, bismuth, cerium and alkali metals may be added to the catalyst as additives. Preferably one or more additives are added to the catalyst which are selected from silver, alkali metals, gold and thallium. The most preferred additive utilized is silver. These additives may be introduced to the catalyst by conventional procedures.

The catalyst carrier may be formed of any catalyst carrier material with a surface area less than about 250 m²/g, such as alumina, zinc oxide, nickel spinel, titania, magnesium oxide and cerium oxide. In a preferred embodiment, the catalyst carrier is formed from alpha

alumina. The surface area of the catalyst carrier is preferably from about 1 to about 250 m²/g and more preferably from about 1 to about 75 m²/g. Its pore volume is preferably from about 0.2 to about 0.7 cc/g. The catalyst carrier can be formed in any suitable size and shape. Preferably it is formed as particles from about 2 to about 6 millimeters in diameter, which are formed into shapes, such as spherical, cylindrical, trilobed and the like. In a more preferred embodiment the catalyst carrier is formed in a spherical shape.

The palladium can be added to the catalyst carrier by any conventional procedure. The presently preferred procedure requires impregnating the catalyst carrier with an aqueous solution of a palladium salt, such as palladium chloride or palladium nitrate, preferably palladium chloride. The extent of penetration of the palladium into the carrier can be controlled by adjustment of the pH of the solution. In a preferred embodiment, the depth of penetration of the palladium salt is controlled such that approximately 90 percent of the palladium salt is contained within 250 microns of the surface of the catalyst carrier. Any suitable method can be used to achieve the preferred palladium penetration, such as is disclosed in U.S. Patent Nos. 4,484,015 and 4,404,124. After palladium impregnation, the impregnated catalyst composition is calcined at a

temperature from about 400 to about 600 degrees C. for about one hour.

Once the palladium-impregnated catalyst composition has been calcined, additives may be added to the catalyst. In one preferred embodiment the additional additive is a metallic additive, preferably an alkali metal, gold, silver and/or thallium additive, and most preferably a silver additive which is impregnated in the form of a salt solution. For example, when silver is utilized the preferred salt is silver nitrate. The palladium/metallic additive impregnated catalyst material is then calcined at a temperature from about 400 to about 600 degrees C. for about one hour.

In an alternative embodiment the additive material and the palladium salt can be co-impregnated and calcined.

The amount of the palladium present after drying is preferably from about 0.001 to about 0.028 weight percent, more preferably 0.01 to about 0.02 weight percent, based on the total weight of the catalyst. When silver is used as an additive, the amount of silver present on the catalyst after drying is preferably from about 0.04 to about 1.0 percent, more preferably 0.04 to 0.12 weight percent based on the total weight of the catalyst. The ratio of the silver to palladium on a by-weight basis is preferably from about 2.1 to about 20.1, more preferably 2:1 to about 6.1, and most

preferably from about 12:1 to about 20:1. It is preferred to employ an aqueous silver nitrate solution in a quantity greater than is necessary to fill the pore volume of the catalyst.

5 The metals contained in the palladium or metal additive/palladium catalyst precursor are then reduced. To reduce the catalyst, it is treated with hydrogen during a heating step. The temperature of this heating step is from about 200 to about 1000°F (93 to about 537°C), preferably 200 to 900°F (93 to about 482°C). The catalyst is heated at the preferred temperature for about 1 to 5 hours, preferably 1 to 3 hours.

10 Following drying and reducing of the catalyst, it is important that the reduced catalyst be stored under a non-oxidizing atmosphere to prevent reoxidation. The term "non-oxidizing atmosphere" refers to gases which do not react with the species present in the reaction environment to reoxidize the metals. The preferred non-oxidizing gases include carbon dioxide, nitrogen, helium, neon, and argon with carbon dioxide and nitrogen more preferred. Air and oxygen are not appropriate because they reoxidize or deactivate the hydrogenation catalyst. Once the reduced catalyst is placed under a non-oxidizing gas, it is loaded into individual containers. The individual containers are then purged with the same or a different non-oxidizing gas

15
20
25

and sealed to prevent contact of the catalyst material with a reoxidizing environment. The sealed catalyst container is then ready for shipment to the reactor site for loading into the reactor. In one example the reduced catalyst is loaded in a conventional container under carbon dioxide or nitrogen. The container is then wrapped securely with a plastic wrap material that is air impermeable.

In use, the catalyst is placed in a reactor and the selective hydrogenation reaction is immediately begun. By use of the catalyst of the invention, it is not necessary to reduce the catalyst in situ before hydrogenation of the compounds in the feed stream. Accordingly, selective hydrogenation of compounds, such as a acetylene, can immediately begin. Such selective hydrogenation occurs when a gas stream containing primarily hydrogen, ethylene, acetylene and carbon monoxide is passed over the catalyst of the invention. During this process the inlet temperature of the feed stream is raised to a level sufficient to hydrogenate the acetylene. Generally, this temperature range is from about 35° C. to about 100° C. Any suitable reaction pressure can be used. Generally, the total pressure is in the range of about 100 to 1000 psig (700 + 7000 KPa) with the gas hourly space velocity (GHSV) in the range of about 1000 to about 14000 liters per liter of catalyst per hour.

It has been surprisingly discovered that the prereduced catalyst of the invention performs better than a catalyst with a similar composition which is activated in situ under feed stock. For example, it has been surprisingly discovered that catalysts which are reduced in hydrogen ex situ and then shipped to the reactor under a non-oxidizing gas have a higher selectivity and better activity than catalysts which are merely activated in situ with feed stock.

It has also been surprisingly discovered that the prereduced catalyst of the invention performs better than a conventional catalyst which is activated with feed, especially when the feed stream has a relatively high concentration of carbon monoxide. Further, it has been surprisingly discovered that the prereduced catalyst of the invention performs better than catalysts with a similar composition which are activated under feed for both front-end and tail-end hydrogenation reactions. An important feature of the invention is the ability of the prereduced catalyst to perform well under high GHSV condition, as high as 12,000 GHSV. Conventional catalysts reduced under feed do not perform as well under these conditions.

EXAMPLES

Example 1 - Invention

A commercial catalyst was acquired from Süd-Chemie Inc.

with a product name of G83A. It comprised an alumina carrier onto which a palladium additive had been added and contained approximately 0.018 percent by weight palladium and about 99 percent weight alumina. It had a BET surface area of 3.7 m²/g. Approximately 25 ccs of the catalyst were placed in a catalyst bed which was purged with nitrogen. The catalyst bed was gradually heated to 200°F (93°C). Once this temperature was reached, the nitrogen was discontinued and hydrogen was introduced into the chamber for at least 60 minutes to reduce the catalyst. Upon completion of the reduction cycle, nitrogen was again introduced into the bed and it was cooled to room temperature. The reduced catalyst was kept under nitrogen atmosphere and loaded into an individual container. This container was purged with nitrogen gas and then sealed to prevent contact with air until it was tested.

Comparative Example 2

A catalyst with the same composition as the catalyst of Example 1 was acquired from Süd-Chemie Inc. It was not reduced prior to testing.

Example 3 - Invention

A commercial catalyst designated as G83C was acquired from Süd-Chemie Inc. It was a palladium catalyst onto which

silver had been added as an additive. It contained 0.018 weight percent palladium and 0.07 weight percent silver on an alumina carrier. It had a BET surface area of about 3.7 m²/g. The catalyst was placed in a bed and purged with nitrogen while the bed was heated to 200°F (93°C). Once that temperature was reached, the nitrogen was discontinued and hydrogen was introduced into the reaction chamber for at least 60 minutes to reduce the catalyst. Upon completion of the reduction cycle, nitrogen was introduced into the bed as it was cooled to room temperature. The reduced catalyst was loaded into an individual container and kept under a nitrogen atmosphere. The container was purged with nitrogen gas and then sealed to prevent contact with air until it was tested.

Comparative Example 4

An additional quantity of the catalyst material of Example 3 was acquired. However, it was not reduced in the manner of Example 3 prior to testing.

Example 5 - Invention

A reduced catalyst was prepared in the same manner as described in Example 3 except the purging gas was carbon dioxide rather than nitrogen.

Example 6 - Invention

A commercial catalyst designated as G58D was acquired from Süd-Chemie Inc. It was a palladium catalyst containing a silver additive. This catalyst contained 0.018 weight percent palladium and 0.012 weight percent silver on an alumina carrier and had a BET surface area of about 3.7 m²/g. The catalyst was reduced and placed in a sealed container under nitrogen in the same manner as described in Example 1, except it was reduced at a temperature of 100°F (38°C).

Example 7 - Invention

The same process as described in Example 6 was conducted on another sample of the catalyst of Example 6 except the temperature of reduction was 150°F (65°C).

Example 8 - Invention

The same process as described in Example 6 was conducted on another sample of the catalyst of Example 6 except the temperature of reduction was 200°F (93°C).

Example 9 - Invention

The same process as described in Example 6 was conducted on another sample of the catalyst of Example 6 except the temperature of reduction was 400°F (204°C).

Example 10 - Invention

The same process as described in Example 6 was conducted on another sample of the catalyst of Example 6 except the temperature of reduction was 700°F (371°C).

5

Comparative Example 11

Another sample of the same catalyst as was used in Examples 6-10 was acquired. However, it was not reduced prior to testing.

10

Example 12 - Invention

A palladium/silver catalyst on alumina carrier designated as G58E was acquired from Süd-Chemie Inc. It contained 0.047 weight percent palladium and 0.282 weight percent silver on an alumina carrier and had a BET surface area of about 150 m²/g. The catalyst was reduced and placed in a sealed container in the same manner as described in Example 1 except the temperature of reduction was 140°F (60°C).

15

20

Example 13 - Invention

The same catalyst as in Example 12 was reduced using the same process as disclosed in Example 12 except that it was reduced for 3 hours at 400°F (204°C).

25

Example 14 - Invention

The same catalyst as in Example 12 was reduced using the same process as disclosed in Example 12 except that it was reduced for 3 hours at 600°F (315°C).

5

Example 15 - Invention

The same catalyst as in Example 12 was reduced using the same process as disclosed in Example 12 except that it was reduced for 3 hours at 800°F (427°C).

10

Comparative Example 16

Another sample of the same catalyst as was used in Examples 12-15 was acquired. However, it was not reduced prior to testing.

15

TABLES**Table 1**

The catalysts of inventive Examples 1, 3 and 5 and Comparative Examples 2 and 4 were tested using a laboratory simulated feed stream in a front-end ethylene purification reactor that employed de-ethanizer separation technology in front of the selective hydrogenation reactor. A moderate GHSV space velocity of 7000 was used at a pressure of 500 psig (3500 KPa) 25 ccs of the catalyst sample were placed in a catalyst bed for testing. The catalyst sample was evaluated in a bench scale 3/4 in. I.D. reactor tube.

20

25

Simulated process feed streams were prepared for catalyst evaluation. The feed streams comprised 1 percent C_2H_6 , 45 percent C_2H_4 , 2800 ppm C_2H_2 , 20 percent H_2 and 250 to 300 ppm CO with the remaining gas comprising CH_4 . The catalysts were tested for 8 hours. Temperature was gradually increased, starting at 87°F (30.5°C). Data was taken every twenty minutes at 4°F (2°C) intervals as the temperature increased. The clean-up temperature (T_1) when exit C_2H_2 level was < 25 ppm was noted. The temperature was increased past T_1 until "runaway" occurred (T_2), i.e. when > 4% hydrogen loss occurred. This temperature minus T_1 was a measure of the selectivity of the catalyst. Higher $T_2 - T_1$ indicates greater selectivity and better thermal stability. The results of the testing are shown in the following Table.

Run	Catalyst	T_1 (°F)	T_2 (°F)	$T_2 - T_1$	Selectivity at T_1
Example 1 (Invention)	G83A (SCI) Pd/Al ₂ O ₃ Reduced in 100% H ₂ at 200°F (93°C) for 1 hour, stabilized in N ₂	114	128	14	11%
Comparative Example 2	G83A (SCI) Pd/Al ₂ O ₃	140	150	10	3%
Example 3 (Invention)	G83C (SCI) Pd/Ag/Al ₂ O ₃ Reduced in 100% H ₂ at 200°F (93°C) for 1 hour, stabilized in N ₂	106	124	18	31.9%
Comparative Example 4	G83C (SCI) Pd/Ag/Al ₂ O ₃	103	107	4	-174.7%
Example 5 (Invention)	G83C (SCI) Pd/Ag/Al ₂ O ₃ Reduced in 100% H ₂ at 200°F (93°C) for 1 hour, stabilized in CO ₂	106	122	16	-24.8%

This data clearly shows that the catalysts of the invention (Examples 1, 3 and 5) have greater selectivity than the catalysts of Comparative Example 2. (The greater the value of the $T_2 - T_1$, the greater the selectivity of the catalyst.) Examples 3 and 5 also exhibited higher selectivity than Comparative Example 4 as shown by the greater value for $T_2 - T_1$.

Table II

This Table shows the performance of the catalyst of the invention under higher GHSV conditions. A de-ethanizer feed was tested at a space velocity of 12000 GHSV. The feed contained the same composition of feed gases as was present in Table I.

Run	Catalyst	T_1 (°F)	T_2 (°F)	$T_2 - T_1$	Selectivity at T_1
Example 1 (Invention)	G83A (SCI) Pd/Al ₂ O ₃ Reduced in 100%H ₂ at 200°F (93°C) for 1 hour, stabilized in N ₂	124	136	12	-40%
Comparative Example 2	G83A (SCI) Pd/Al ₂ O ₃	143	148	5	-123%
Example 3 (Invention)	G83C (SCI) Pd/Ag/Al ₂ O ₃ Reduced in 100%H ₂ at 200°F (93°C) for 1 hour, stabilized in N ₂	126	135	9	-11.6%
Comparative Example 4	G83C (SCI) Pd/Al ₂ O ₃	N/A	124	---	---

This Table clearly shows a greater selectivity and

stability of the inventive example, Example 1, over the comparative example, Comparative Example 2. The non-reduced catalyst could not significantly remove C_2H_2 from the feed stream under these conditions. The lower temperature of T_1 obtained with Example 1, in comparison to Comparative Example 2 also indicates a higher activity level, as shown by the lower clean-up temperature for the inventive catalyst. The non-reduced silver-promoted catalyst of Example 4 could not significantly remove C_2H_2 from the feed stream under these conditions. The silver-promoted catalyst of Example 3 successfully removed acetylene even at this high space velocity.

Table III

The purpose of this Table is to show the performance of the catalyst of the invention with different types of feed stock, particularly with a high carbon monoxide concentration. The feed stream contained 1 percent C_2H_6 , 18 percent C_2H_4 , 14 ppm C_2H_2 , 20 percent H_2 , 3 percent C_3H_6 , 0.02 percent C_3H_8 , 8060 ppm CO and the remaining portion CH_4 .

Run	Catalyst	T_1 (°F)	T_2 (°F)	$T_2 - T_1$	Selectivity at T_1
Example 1 (Invention)	G83A (SCI) Pd/Al ₂ O ₃ Reduced in 100% H ₂ at 200°F (93°C) for 1 hour, stabilized in N ₂	140	161	21	7%
Comparative Example 2	G83C (SCI) Pd/Al ₂ O ₃	151	159	8	-28%

As can be seen from Table III, the catalyst of the invention (Example 1) outperformed the currently available non-reduced comparative catalyst (Comparative Example 2) by exhibiting higher selectivity and stability (T_2-T_1). (The higher activity for the invention is measured by the lower value of T_1 .) This is especially impressive considering the high quantity of CO present (8060 ppm).

Table IV

Table IV shows another example of the performance of the catalyst of the invention, both with and without the addition of silver as a promoter. The feed stream is contained in a front-end reactor system utilizing deproponizer separation before the C_2H_2 reactor. The feed contained 21 percent CH_4 , 1 percent C_2H_6 , 53 percent C_2H_4 , 0.03 percent C_3H_8 , 6 percent C_3H_6 , 0.05 percent propadiene, 0.044 percent C_2H_2 , 0.16 percent methylacetylene, 18.5 percent H_2 , 0.05 percent CO and the remaining portion CH_4 .

Run	Catalyst	T ₁ (°F)	T ₂ (°F)	T ₂ -T ₁	Selectivity at T ₁
Example 1 (Invention)	G83A (SCI) Pd/Al ₂ O ₃ Pre-reduced in 100%H ₂ at 200°F (93°C) for 1 hour, stabilized in N ₂	100	156	56	72%
Comparative Example 2	G83A (SCI) Pd/Al ₂ O ₃	136	166	30	51%
Example 3 (Invention)	G83C (SCI) Pd/Ag/Al ₂ O ₃ Pre-reduced in 100%H ₂ at 200°F (93°C) for 1 hour, stabilized in N ₂	126	154	28	-85%
Comparative Example 4	G83C (SCI) Pd/Ag/Al ₂ O ₃	127	147	20	-290%

As can be seen from Table IV, the catalyst of the invention (Example 1) outperformed the non-reduced comparative catalyst (Comparative Example 2) in selectivity (higher T₂ - T₁) and stability. The lower value of T₁ of the inventive Example 1 indicates higher activity.

Table V

The purpose of Table V is to show the impact of different temperatures of reduction on the performance of the various catalysts. The feed stream is comprised of a de-ethanizer feed under 7000 GHSV consisting of one percent C₂H₆, 45 percent C₂H₄, 2800 ppm C₂H₂, 20 percent H₂, 250-300 ppm CO and the remaining portion CH₄.

Run	Catalyst	T ₁ (°F)	T ₂ (°F)	T ₂ -T ₁
Example 6 (Invention)	G58D 100% hydrogen reduction at 100°F (38°C)	123	141	18
Example 7 (Invention)	G58D 100% hydrogen reduction at 150°F (68°C)	127	141	14
Example 8 (Invention)	G58D 100% hydrogen reduction at 200°F (93°C)	137	149	12
Example 9 (Invention)	G58D 100% hydrogen reduction at 400°F (204°C)	127	140	13
Example 10 (Invention)	G58D 100% hydrogen reduction at 700°F (371°C)	N/A*	147	N/A*
Comparison Example 11	G58D no hydrogen reduction	103	110	7

This Table shows that the performance of the catalysts of the invention (Examples 6-10) is better than that of a catalyst which is not prereduced (Comparison Example 11). The optimized performance was present in Example 6 which was prereduced at 100°F (38°C).

Table VI

The process used for the production of the catalyst of the invention is also useful for tail-end purification as is shown in the Table VI. The tail-end feed was comprised of 1 percent C₂H₂, 1.5 percent H₂ with the balance being C₂H₄. The catalysts of the invention were prereduced at various temperatures and over various times under a space velocity of 5000 GHSV.

Run	Catalyst	%C ₂ H ₂ conversion	% Selectivity	Polymer formed
Example 12 (Invention)	G58E Reduced in 100% H ₂ for 1 hour at 140°F (60°C)	97.3	38.8	0.9430
Example 13 (Invention)	G58E Reduced in 100% H ₂ for 3 hours at 400°F (204°C)	94.7	40.4	0.4419
Example 14 (Invention)	G58E Reduced in 100% H ₂ for 3 hours at 600°F (315°C)	94.4	39.0	0.2907
Example 15 (Invention)	G58E Reduced in 100% H ₂ for 3 hours at 800°F (427°C)	95.4	48.8	0.3759
Comparative Example 16	G58E	92.1	21.1	0.9414

Upon review of the Table, it is clear that the catalyst of the invention (Examples 12-15) showed improved performance in situ as each had a higher selectivity compared to the commercially available catalyst of Comparative Example 16. A noticeable reduction in polymer formation was also evidenced in inventive Examples 13-15.

In addition, each of the examples showed that the catalysts produced by the process of the invention which was prereduced performed better than catalysts activated with feed stock in situ even when there was substantial hydrogen and carbon monoxide present in the in situ feed stream.

It will be apparent from the foregoing that while particular forms of the invention have been illustrated,

various modifications can be made without departing from the scope of the invention.

11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000
1001
1002
1003
1004
1005
1006
1007
1008
1009
1010
1011
1012
1013
1014
1015
1016
1017
1018
1019
1020
1021
1022
1023
1024
1025
1026
1027
1028
1029
1030
1031
1032
1033
1034
1035
1036
1037
1038
1039
1040
1041
1042
1043
1044
1045
1046
1047
1048
1049
1050
1051
1052
1053
1054
1055
1056
1057
1058
1059
1060
1061
1062
1063
1064
1065
1066
1067
1068
1069
1070
1071
1072
1073
1074
1075
1076
1077
1078
1079
1080
1081
1082
1083
1084
1085
1086
1087
1088
1089
1090
1091
1092
1093
1094
1095
1096
1097
1098
1099
1100
1101
1102
1103
1104
1105
1106
1107
1108
1109
1110
1111
1112
1113
1114
1115
1116
1117
1118
1119
1120
1121
1122
1123
1124
1125
1126
1127
1128
1129
1130
1131
1132
1133
1134
1135
1136
1137
1138
1139
1140
1141
1142
1143
1144
1145
1146
1147
1148
1149
1150
1151
1152
1153
1154
1155
1156
1157
1158
1159
1160
1161
1162
1163
1164
1165
1166
1167
1168
1169
1170
1171
1172
1173
1174
1175
1176
1177
1178
1179
1180
1181
1182
1183
1184
1185
1186
1187
1188
1189
1190
1191
1192
1193
1194
1195
1196
1197
1198
1199
1200
1201
1202
1203
1204
1205
1206
1207
1208
1209
1210
1211
1212
1213
1214
1215
1216
1217
1218
1219
1220
1221
1222
1223
1224
1225
1226
1227
1228
1229
1230
1231
1232
1233
1234
1235
1236
1237
1238
1239
1240
1241
1242
1243
1244
1245
1246
1247
1248
1249
1250
1251
1252
1253
1254
1255
1256
1257
1258
1259
1260
1261
1262
1263
1264
1265
1266
1267
1268
1269
1270
1271
1272
1273
1274
1275
1276
1277
1278
1279
1280
1281
1282
1283
1284
1285
1286
1287
1288
1289
1290
1291
1292
1293
1294
1295
1296
1297
1298
1299
1300
1301
1302
1303
1304
1305
1306
1307
1308
1309
1310
1311
1312
1313
1314
1315
1316
1317
1318
1319
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344
1345
1346
1347
1348
1349
1350
1351
1352
1353
1354
1355
1356
1357
1358
1359
1360
1361
1362
1363
1364
1365
1366
1367
1368
1369
1370
1371
1372
1373
1374
1375
1376
1377
1378
1379
1380
1381
1382
1383
1384
1385
1386
1387
1388
1389
1390
1391
1392
1393
1394
1395
1396
1397
1398
1399
1400
1401
1402
1403
1404
1405
1406
1407
1408
1409
1410
1411
1412
1413
1414
1415
1416
1417
1418
1419
1420
1421
1422
1423
1424
1425
1426
1427
1428
1429
1430
1431
1432
1433
1434
1435
1436
1437
1438
1439
1440
1441
1442
1443
1444
1445
1446
1447
1448
1449
1450
1451
1452
1453
1454
1455
1456
1457
1458
1459
1460
1461
1462
1463
1464
1465
1466
1467
1468
1469
1470
1471
1472
1473
1474
1475
1476
1477
1478
1479
1480
1481
1482
1483
1484
1485
1486
1487
1488
1489
1490
1491
1492
1493
1494
1495
1496
1497
1498
1499
1500
1501
1502
1503
1504
1505
1506
1507
1508
1509
1510
1511
1512
1513
1514
1515
1516
1517
1518
1519
1520
1521
1522
1523
1524
1525
1526
1527
1528
1529
1530
1531
1532
1533
1534
1535
1536
1537
1538
1539
1540
1541
1542
1543
1544
1545
1546
1547
1548
1549
1550
1551
1552
1553
1554
1555
1556
1557
1558
1559
1560
1561
1562
1563
1564
1565
1566
1567
1568
1569
1570
1571
1572
1573
1574
1575
1576
1577
1578
1579
1580
1581
1582
1583
1584
1585
1586
1587
1588
1589
1590
1591
1592
1593
1594
1595
1596
1597
1598
1599
1600
1601
1602
1603
1604
1605
1606
1607
1608
1609
1610
1611
1612
1613
1614
1615
1616
1617
1618
1619
1620
1621
1622
1623
1624
1625
1626
1627
1628
1629
1630
1631
1632
1633
1634
1635
1636
1637
1638
1639
1640
1641
1642
1643
1644
1645
1646
1647
1648
1649
1650
1651
1652
1653
1654
1655
1656
1657
1658
1659
1660
1661
1662
1663
1664
1665
1666
1667
1668
1669
1670
1671
1672
1673
1674
1675
1676
1677
1678
1679
1680
1681
1682
1683
1684
1685
1686
1687
1688
1689
1690
1691
1692
1693
1694
1695
1696
1697
1698
1699
1700
1701
1702
1703
1704
1705
1706
1707
1708
1709
1710
1711
1712
1713
1714
1715
1716
1717
1718
1719
1720
1721
1722
1723
1724
1725
1726
1727
1728
1729
1730
1731
1732
1733
1734
1735
1736
1737
1738
1739
1740
1741
1742
1743
1744
1745
1746
1747
1748
1749
1750
1751
1752
1753
1754
1755
1756
1757
1758
1759
1760
1761
1762
1763
1764
1765
1766
1767
1768
1769
1770
1771
1772
1773
1774
1775
1776
1777
1778
1779
1780
1781
1782
1783
1784
1785
1786
1787
1788
1789
1790
1791
1792
1793
1794
1795
1796
1797
1798
1799
1800
1801
1802
1803
1804
1805
1806
1807
1808
1809
1810
1811
1812
1813
1814
1815
1816
1817
1818
1819
1820
1821
1822
1823
1824
1825
1826
1827
1828
1829
1830
1831
1832
1833
1834
1835
1836
1837
1838
1839
1840
1841
1842
1843
1844
1845
1846
1847
1848
1849
1850
1851
1852
1853
1854
1855
1856
1857
1858
1859
1860
1861
1862
1863
1864
1865
1866
1867
1868
1869
1870
1871
1872
1873
1874
1875
1876
1877
1878
1879
1880
1881
1882
1883
1884
1885
1886
1887
1888
1889
1890
1891
1892
1893
1894
1895
1896
1897
1898
1899
1900
1901
1902
1903
1904
1905
1906
1907
1908
1909
1910
1911
1912
1913
1914
1915
1916
1917
1918
1919
1920
1921
1922
1923
1924
1925
1926
1927
1928
1929
1930
1931
1932
1933
1934
1935
1936
1937
1938
1939
1940
1941
1942
1943
1944
1945
1946
1947
1948
1949
1950
1951
1952
1953
1954
1955
1956
1957
1958
1959
1960
1961
1962
1963
1964
1965
1966
1967
1968
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
1984
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
2024
2025
2026
2027
2028
2029
2030
2031
2032
2033
2034
2035
2036
2037
2038
2039
2040
2041
2042
2043
2044
2045
2046
2047
2048
2049
2050
2051
2052
2053
2054
2055
2056
2057
2058
2059
2060
2061
2062
2063
2064
2065
2066
2067
2068
2069
2070
2071
2072
2073
2074
2075
2076
2077
2078
2079
2080
2081
2082
2083
2084
2085
2086
2087
2088
2089
2090
2091
2092
2093
2094
2095
2096
2097
2098
2099
2100
2101
2102
2103
2104
2105
2106
2107
2108
2109
2110
2111
2112
2113
2114
2115
2116
2117
2118
2119
2120
2121
2122
2123
2124
2125
2126
2127
2128
2129
2130
2131
2132
2133
2134
2135
2136
2137
2138
2139
2140
2141
2142
2143
2144
2145
2146
2147
2148
2149
2150
2151
2152
2153
2154
2155
2156
2157
2158
2159
2160
2161
2162
2163
2164
2165
2166
2167
2168
2169
2170
2171
2172
2173
2174
2175
2176
2177
2178
2179
2180
2181
2182
2183
2184
2185
2186
2187
2188
2189
2190
2191
2192
2193
2194
2195
2196
2197
2198
2199
2200
2201
2202
2203
2204
2205
2206
2207
2208
2209
2210
2211
2212
2213
2214
2215
2216
2217
2218
2219
2220
2221
2222
2223
2224
2225
2226
2227
2228
2229
2230
2231
2232
2233
2234
2235
2